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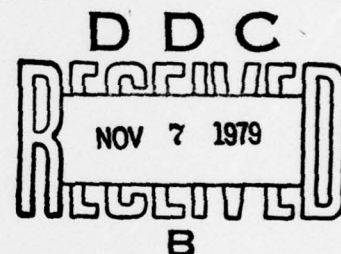
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MEMORANDUM REPORT ARBRL-MR-02953

PROPELLANT COMBUSTION DIAGNOSTICS

Nathan Klein  
George E. Keller

September 1979



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND  
BALLISTIC RESEARCH LABORATORY  
ABERDEEN PROVING GROUND, MARYLAND

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20. Abstract (continued)

some of the needed information. The complexity of the techniques and their level of development varies widely and their potential must be evaluated on a case-by-case basis as to which would be most amenable for use. A large portion of the equipment required for their exploitation is the same so that an effort in the general area of combustion diagnostics by advanced optical methods would make a number of the methods available for evaluation. Ancillary data concerning propellant functioning other than combustion would also become available if such a combustion diagnostics program were actively pursued.



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# TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS . . . . .	5
I. INTRODUCTION . . . . .	7
II. GUN PROPELLANT COMBUSTION . . . . .	9
III. COMBUSTION DIAGNOSTIC TECHNIQUES . . . . .	17
IV. EXPERIMENTAL CONSIDERATIONS . . . . .	33
V. CONCLUSIONS AND RECOMMENDATIONS . . . . .	37
REFERENCES . . . . .	38
DISTRIBUTION LIST . . . . .	41

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## LIST OF ILLUSTRATIONS

Figure	Page
1. A Typical Gun Propellant Charge. . . . .	11
2. Propellant Combustion at Moderate Pressure . . . . .	11
3. Light Scattering . . . . .	21
4. Fluorescence Energy Diagram. . . . .	25
5. Inverse Raman Spectroscopy . . . . .	31
6. Coherent Anti-Stokes Raman Scattering (CARS) . . . . .	32
7. Laser Excited Fluorescence . . . . .	35
8. Inverse Raman Spectroscopy . . . . .	35
9. Coherent Anti-Stokes Raman Spectroscopy. . . . .	36

## I. INTRODUCTION

In the Spring of 1978 a study was initiated at the Ballistic Research Laboratory in the area of combustion diagnostic techniques as they would be applicable to a gun environment. The study was to be relatively brief and therefore qualitative. The object of the work was to review diagnostic techniques that had been used in the past, assess various new techniques that are presently being developed in terms of their potential applicability to gun combustion studies, and estimate what benefits might accrue from exploitation of such techniques. This report is the product of that study.

The study was essentially divided into two parts. The first part was a review of propellant combustion with emphasis on combustion under the conditions existing in a gun. Its purpose was to describe the current state of knowledge and identify those areas where additional information would have major impact on our understanding of the combustion process. We made a conscious effort to keep such review as free as possible from preconceived ideas of what areas of study would be of greatest value. We realized that background and previous work experience would orient our assessment of the needed information to favor science over engineering and probably to favor fundamental over applied science. The second part of the study surveys techniques that either have been used or have potential for use as methods to obtain needed combustion information. We emphasize that the study deals with combustion and combustion diagnostics and not with ballistics. Ballistics should be the ultimate beneficiary of all gun propellant combustion work but ballistics is a highly specialized, applied technology, and its invocation at an early stage results in a level of empiricism that is not conducive to the development of an adequate level of understanding of the combustion processes.

Early in the study it became clear that some reasonably precise limits and definitions were required in order to describe the problem and establish bounds so that the problem could be addressed within the time and personnel limitations imposed. For purposes of this study, we will limit discussion to materials that are used or have potential use as propellants in guns. We will further limit discussion to gun propellants that release energy by way of chemical reaction. We define combustion as the collection of physical and chemical processes that take place in going from the starting materials to the final products and we define a combustion diagnostic technique as any method that permits elucidation of one or more of the physical or chemical processes that occur during combustion.

Combustion diagnostic techniques are probably as well known generally as is combustion itself. One observes that the fire burns more brightly and gives off more heat when the supply of air is improved. Many such observations have been made in a qualitative or semi-qualitative manner and have been widely used to produce better performing combustion systems.

Such observations, however, reveal very little in terms of the details of the combustion process with the result that modifications and improvements in equipment utilizing combustion have been accomplished almost completely by empirical methods. The fact that improvements have been made in machines utilizing combustion, including guns, by empirical methods and that understanding of the processes involved has lagged far behind has often created an attitude that is, of itself, not conducive to the developing of such understanding. The argument advanced possesses a logical flaw but is advanced nonetheless, to wit, guns have been in use for several hundred years without our understanding the processes involved, therefore, such understanding is unnecessary.

Quantitative combustion diagnostic techniques have also been developed. These techniques generally are either active or passive, that is, they either observe the process while it is taking place or they involve sampling combustion products for subsequent analysis with the expectation that the results of such analysis will give insight into events that occurred during combustion. All of the techniques employed to date have limitations, some of which are more severe than others. One question that must be addressed regardless of the diagnostic method used is whether the measurement perturbs the event under study to a point that the measurement no longer represents the true event. If so, the measurement is of very limited value. The use of probes, whether for sampling or for other purposes, has always been criticized because of the possibility of such perturbation. Recently<sup>1</sup>, a number of optical methods have been investigated that hold substantial promise for non-perturbing, detailed, diagnostic measurements of the combustion process as it takes place in various air-breathing engines.

One quickly realizes that combustion of gun propellants differs markedly from combustion in air-breathing engines if for no other reason than that temperatures and pressures are much higher in the practical combustion of a gun propellant. A number of other reasons also exist that reinforce this marked difference and as a result virtually the only non-perturbing diagnostic measurements that have been successfully made in the case of practical gun propellant combustion have been the measurement of pressure as a function of time and high-speed photography. Numerous other diagnostic measurements have been made that used probes of various kinds or required conditions far less severe than those encountered in actual gun use. Such data have been used in developing current propellant combustion models. Advanced diagnostic techniques might be able to provide additional data that would lead to significant improvements in combustion modeling. In a larger sense, a more detailed and accurate description of the combustion process could result in improvements in propellant formulation and utilization in the gun, thus producing major improvements in weapons systems.

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1. *Combustion Measurements*, R. Goulard, ed., Academic Press, New York (1976), pp. 67-283.

## II. GUN PROPELLANT COMBUSTION

A modern, solid, gun propellant is a collection of materials in some predetermined geometric shape that, when ignited, will cause work to be performed in a known manner. The mixture must be stable, by which is meant that after some extended period of storage followed by a return to a uniform set of starting conditions, the mixture will ignite and release energy in a way that will not have been affected by the period of storage. This non-deteriorization of performance imposes both physical and chemical requirements on the propellant. The mixture may not separate into various components which could fractionate into regions of significantly different concentration within the total sample. It may also neither agglomerate nor break up into particles of substantially different size. Such physical changes are known<sup>2</sup> to alter burning characteristics drastically and the propellant is therefore prepared in such manner as to prevent such changes from taking place. Burning characteristics are also known to be strongly affected by the surface area and loading density, that is, the quantity of energetic material per unit chamber volume. Both surface area and loading density are carefully controlled during manufacturing of the propellant charge and should not change in storage. In addition to the physical integrity of the propellant, chemical changes must also be avoided during storage and to this end, stabilizers are frequently added that retard or, more ideally, entirely prevent undesired chemical changes from taking place. Lastly, it has been found that burning characteristics can be altered by the presence of certain materials often called burning rate modifiers, that are themselves neither propellants nor stabilizers. The mixtures in toto, should, when burned, produce a minimum of smoke and little or no solid residue. This rather complex collection of materials, assembled in a fixed size and shape, describes a gun propellant prior to use. Reaction is initiated by some device that introduces enough energy into the propellant to cause combustion to occur.

Gun propellants function by releasing energy, that is, in going from starting material to final products a net release of energy is obtained. The chemical reactions that cause this energy release are usually a rather complex set of oxidations and reductions and conservation laws require that these reactions result in an increase in either temperature, pressure, or both. From practical considerations, the rate of energy release has both upper and lower bounds. If the release rate is too high, temperatures and pressures will develop that exceed the limitations of the containment vessel which will then fail catastrophically. On the other hand, if the release rate is too low, insufficient work will be done on the projectile in a timely manner and the projectile will not achieve the velocity desired. It should also be mentioned that a gun propellant is self-contained so that all of the ingredients necessary for desired reaction sequences are present in the starting materials.

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2. J. Taylor, *Solid Propellant and Exothermic Compositions*, Interscience, New York (1959).

When one considers that a modern gun propellant can reproducibly release heat in excess of  $1 \text{ kJ gm}^{-1}$ , generating temperature in excess of  $2700^\circ\text{C}$ , and pressures exceeding 350 MPa within tens of milliseconds, one realizes quite how unique such material is.

The thermal stability requirements imposed on modern, practical, gun propellants make reaction initiation difficult, a rather severe and controlled thermal impulse being required for proper initiation. Such impulse is delivered by a separate device, called an igniter, that is incorporated in the complete propellant package. The igniter contains a propellant with physical and chemical properties that are often very different from those of the main charge. Ignition of the propellant used in the igniter portion is usually achieved with a much smaller thermal impulse than that necessary for initiation of the main charge. In addition, the rate of energy release, commonly called the burning rate, of the igniter is often markedly different from that of the main charge since its function is to ignite the main charge rather than to accelerate the projectile. Since the quantity of material used in the igniter is substantially less than that of the main charge and is packaged differently, overall thermal stability of the complete propellant package is maintained.

Reactions in the igniter are initiated by energy release in a third device, called a primer. The primer is generally ignited by either mechanical shock or some small amount of heat obtained by applying an electric current to a length of resistance wire. The energy required for initiation of reaction in the primer is quite small and safety is retained by using a small quantity of material in the primer and by keeping this material well shielded from its surroundings.

Generally, the primer contains so little material that the effect of its combustion is not seen when studying reactions of the main charge. The same cannot be said for the igniter, however. Ignition and subsequent combustion of the main propellant charge is often strongly dependent on both the composition and the mechanical design of the igniter and gun propellant combustion studies can, and often do, become studies of the ignition and combustion of two propellants that, for part of the combustion cycle, are burning simultaneously. This added complexity is far from trivial and when one considers that the propellant used in igniters is most often black powder, the magnitude of the problem becomes clear. Black powder, a mixture of saltpeter, charcoal, and sulfur, has been used in guns for over 600 years and its origins date back to antiquity. In spite of its long history and extensive use, the combustion of black powder is not yet adequately understood and techniques for its preparation and employment are still largely empirical. A stylized drawing of a propellant charge as might be used in a medium caliber gun is shown in Figure 1. Both the igniter and the main charge are shown.

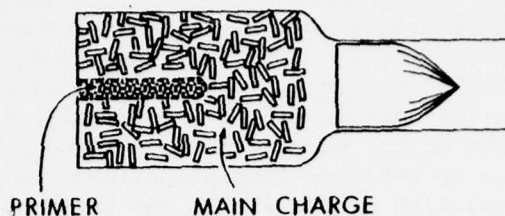


Figure 1. A Typical Gun Propellant Charge

Ignition and combustion of the igniter causes a mixture of hot gases and, in some cases, burning particles to come in contact with the main propellant charge and this contact results in ignition and subsequent combustion. The main propellant charge falls into one of three categories, if one limits discussion to propellants used in guns by the U.S. Army at the present time. These categories are the single, double, and triple base propellants, all of which contain nitrocellulose (NC) or guncotton, a material prepared by the action of nitric and sulfuric acids on cellulose. In addition to NC, the double base propellants contain nitroglycerin (NG), and the triple base propellants contain nitroguanidine (NGu) in addition to the NC and NG. A variety of stabilizers, plasticizers and colorants are also frequently present in small amounts. As might be expected, the chemical composition of the propellant strongly influences its combustion, in terms of gas evolved and the rate of gas evolution.

In addition to the effect of chemical composition, geometrical factors play major roles in combustion. Observation of the gross combustion process reveals why such should be the case<sup>3</sup>. What one sees at the surface is either a melting or decomposition that results in a froth or foam. This region develops into a zone in which reactions are taking place that give rise to gaseous products. These gaseous products subsequently react producing the luminosity commonly associated with combustion. A burning propellant grain is shown in Figure 2.

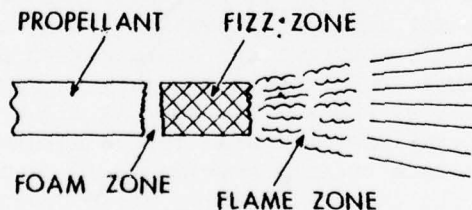


Figure 2. Propellant Combustion at Moderate Pressure

3. Symposium on Kinetics of Propellants, J. Phys. Chem. 54, 847 (1950).

In Figure 2, the foam, fizz, and flame zones appear as separate regions. In reality, no distinct boundary separates these regions. As pressure is increased in the system, these zones become smaller and, at gun pressures, have dimensions in fractions of a millimeter if they exist at all. The diagnostic problem posed by these very small and closely spaced reaction zones will be addressed subsequently. This reaction sequence, originating as it does at the surface of the propellant, will take place at a rate that is dependent on the surface area. Profound differences in gas evolution rates can be obtained from propellants of the same chemical composition by manipulation of the shapes and sizes in which the propellant is produced<sup>4</sup>. Whether such changes are also due to changes in the chemical reactions that are taking place is not presently known. The interplay of physical and chemical processes are, in many cases, virtually inseparable. For example, the transfer of heat from regions of rapid chemical reaction back to the starting material can often be the controlling process in combustion since such heat transfer would be instrumental in generating the reactants that undergo the rapid chemical reactions observed. Independent observation of heat transfer may or may not be of value in the example cited, and the ability to make such a measurement without significantly perturbing the system, is far from certain. Conversely, a description of the chemical reactions, obtained under precise laboratory conditions, may be of little use because the conditions employed are too far removed from conditions existing in actual use either because the necessary conditions are unknown or are unobtainable in the laboratory. Still an additional complication could stem from the possibility that the various physical and chemical processes are nonlinearly coupled. If this is indeed the case, then separation of the various processes must be avoided in order to obtain valid data. The complexity of the research problem engendered by this latter possibility is of such magnitude that the probability of obtaining pertinent, precise, analytical data becomes exceedingly small.

It should be noted that knowledge of the identity and reactivity of all of the chemical species involved in the ignition and combustion of a propellant is not, of itself, sufficient to describe the event being studied. From the composition and mechanical assembly of a modern gun propellant, it would seem obvious that a large number of reactions could take place either simultaneously or sequentially and a number of these reactions could involve one or more of the same starting materials. If such were the case, then geometrical considerations take on an added significance because reactant concentrations could vary drastically from one location to another. This would result not only in variation in reaction rate with concentration and temperature, as might be expected from simple kinetics considerations, but also in the nature of the reaction itself. An adequate attack on this problem would require not only an accurate description of the chemical species being produced and the quantities of heat evolved but also such description in space and time.

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4. J. Corner, *Theory of the Interior Ballistics of Guns*, J. Wiley and Sons, New York (1950).

A great deal of excellent work has been done on the thermochemistry of propellant combustion. Corner, in his classic text<sup>4</sup>, summarizes much of the important work to 1950, and significant advances have been made since then<sup>5</sup>. However, it must be remembered that a fundamental concept in all classical thermodynamics is independence of path, that is, a system at equilibrium may be converted to a second system, also at equilibrium, by any means desired. The thermodynamic values associated with such conversion will be totally independent of the path chosen. Using this concept, accurate descriptions of the initial and final state of a system permits calculation of all of the thermodynamic quantities, and in like manner, an accurate description of the initial state and the thermodynamic quantities make possible an accurate description of the final state. Classical thermodynamics is unable to provide any information regarding the time required to achieve equilibrium or what the composition of a system might be during the period of change. In spite of such severe limitations, substantial success has been achieved using classical thermodynamics to describe portions of propellant combustion processes.

Previous comments concerning the very small sizes of reaction zones would seem to oppose the concept of equilibrium as required by classical thermodynamics, since it is difficult to conceive that a rapidly changing system with such small dimensions could even approach, never mind achieve, equilibrium. The successful application of thermochemistry to practical combustion problems demands resolution of this apparent anomaly. One notes that thermochemistry describes only portions of the combustion processes. Measurement have been made over the years that attempt to characterize propellants as to their rate of energy release. Such quantities as linear and mass burning rate and relative quickness are examples of this type of reaction rate characterization. Definition of these combustion rate characteristics are often quite arbitrary and are interpreted with difficulty. Burning rate usually means the rate of consumption of a propellant sample under a given set of conditions. It does not necessarily mean the rate at which propellant is converted from starting material to stable products. Quickness generally means the rate of gas production during some portion of the combustion cycle. The kind of information provided by measurements of burning rate and quickness are quite important for the proper utilization of propellants in guns. Thermochemical considerations do not lead to any predictive capability regarding such rate associated phenomena and, at present, no means exist for predicting such rates other than purely empirical, analogous reasoning.

There is a rather strong relationship between thermochemical properties and kinetic parameters used to describe reaction rates. As an example, the equilibrium constant,  $K$ , for a given reaction can be expressed as:

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5. E. Freedman and R. D. Anderson, "Thermodynamic Calculation on Propellant and Black Powder", pp. 13-18 in "1975 Annual Review of ARMCOM Program, The Fundamentals of Ignition and Combustion", E. Freedman and K. J. White, ed, BRL Report No. 1883, May 1976. (AD #B011644L)

$$K = \frac{k_1}{k_{-1}}$$

where  $k_1$  is the reaction rate constant for the forward reaction and  $k_{-1}$  is the rate constant for the reverse reaction. The equilibrium constant can also be expressed using thermodynamic quantities as:

$$\Delta G^\circ = -RT \ln K$$

where  $\Delta G^\circ$  is the standard free energy,  $R$  is the gas constant and  $T$  is the absolute temperature. By definition:

$$\Delta G^\circ \equiv \Delta H^\circ - T\Delta S^\circ$$

where  $\Delta H^\circ$  is the change in standard enthalpy and  $\Delta S^\circ$  is the standard entropy change. The Arrhenius parameters,  $A$  and  $E$ , in the reaction rate equation:

$$k = A e^{-E/RT}$$

where  $A$  is the frequency factor and  $E$  is activation energy are related to the thermochemical quantities  $\Delta H^\circ$  and  $\Delta S^\circ$  by the equations:

$$\Delta S_1^\circ = R \ln \frac{A_1}{A_{-1}}$$

and 
$$\Delta H_1^\circ = E_1 - E_{-1}$$

using the same subscript convention as above. For gas phase reactions, these thermochemical and kinetic interrelations have been developed into predictive methods by Benson and his coworkers<sup>6</sup>, and have been successfully applied to some rather complex reaction systems. Treatment of reactions in condensed phases has not yet reached the level of development that exists for reactions in the gas phase but there is no fundamental limitation that precludes such development. There are some important differences between gas and condensed phase reactions that make the development of such predictive methods much more than simple extensions of technique, however. Such matters as a proper description of the activated complex in condensed phase reactions and the influence of a

6. S. W. Benson, Thermochemical Kinetics, J. Wiley and Sons, New York (1968).

solvent cage on species reactivity must be addressed before an adequate predictive capability will be realized.

Presently used gun propellants are chemically very similar. One notes that the significant ingredients in all cases consist only of the elements carbon, hydrogen, oxygen, and nitrogen and that all are non-ionic, organic compounds. Bond energies for all of the possible single, covalent, bonds found in these ingredients range from 110.6 kcal mole<sup>-1</sup> for the O-H bond to 57.0 kcal mole<sup>-1</sup> for the N-O bond<sup>7</sup> with a mean value of  $87.1 \pm 16.8$  kcal mole<sup>-1</sup>. Since essentially similar structures will decompose and essentially similar product gases (N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CO, etc.) will be formed, it would be reasonable to expect that both the thermochemistry and the reaction kinetics vary in a more-or-less parallel fashion over a fairly narrow range. This is especially the case if one considers reaction kinetics on a global or at most, semi-global scale. The apparant reactions now considered are the sum of numbers of reactions and the kinetic parameters all tend toward a mean value so that the role of reaction pathway appears to become less important. This rationale loses validity if compounds of different chemical structure such as ionic or inorganic compounds are considered as propellant ingredients and the predictive capability of thermodynamics should weaken, possibly to the level of non-acceptability because the thermochemistry-kinetics parallelism would no longer be the same. Some evidence for this breakdown may possibly be seen in the nitramine containing propellants and in compositions containing significant quantities of inorganic salts such as ammonium nitrate. The ignition and combustion characteristics of these mixtures are quite different from those of the more usual single, double, or triple base propellants. Unfortunately, some of the physical characteristics of these materials are also different from those of the more conventional gun propellants as that cause-and-effect arguments are not easily made. In any case, presently used measurement and computational techniques are inadequate for prediction of ignition and combustion characteristics.

The preceding discussion centered on equilibrium thermodynamics and the fact that its use within narrow constraints would provide no information either negative or positive concerning the role of reaction kinetics in the system being studied. In recent years non-equilibrium thermodynamics has begun to receive some well deserved attention. The comment is made by de Groot<sup>8</sup> that equilibrium thermodynamics could more appropriately be called thermostatics whereas irreversible processes require dynamics for adequate explanation. There are numerous examples of irreversible processes such as diffusion, heat conduction, electrical conduction, and, most assuredly, combustion. A common consideration in all irreversible processes is the spatial and temporal variation in the thermodynamic quantities and, in a more general case, simultaneous

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7. S. F. Sarner, *Propellant Chemistry*, Reinhold, New York (1966), p. 64.

8. S. R. de Groot, *Thermodynamics of Irreversible Processes*, North Holland Publishing Co., Amsterdam (1951), p. 1.

variation of both chemical entities and the thermodynamic quantities of these chemical entities. The problem is made more complex by including for consideration properties that are cross phenomena, that is, a property that is the combination of other properties. Thermal diffusion is an example of such a cross phenomenon, the transport of matter by temperature gradients being called the Soret effect, the transport of heat by concentration gradients is the Dufour effect, etc. There is no reason, a priori, to assume that such cross phenomena are linear sums of the individual processes and, in fact, it would seem more realistic to expect that in multi-component systems such cross phenomena would appear non-linear.

Following the pioneering work of Prigogine<sup>9</sup>, non-equilibrium thermodynamics has been developed and applied to a variety of homogeneous and heterogeneous systems<sup>10</sup>. It would seem worthwhile to consider propellant combustion qualitatively in light of irreversible thermodynamics. Assume that the propellant sample is a homogeneous mixture of several materials with an abrupt discontinuity at the grain boundary. For simplicity one can also assume that combustion has been initiated by some instantaneous thermal input at the grain boundary. This thermal input causes exothermic chemical reactions to take place. Both heat and a variety of reaction products are created at the boundary. The products transport some heat away but some portion is absorbed by the propellant that has not yet reacted. This material will now react at a different temperature and, hence, at a different rate from the sample preceding so that reaction products and heat will be produced at a different rate which will cause a change to be observed in transport properties. Assuming nothing else were to occur, a quasi-equilibrium could be achieved where the rate of change in both heat and material transport would approach zero. In a gun such cannot be the case because the system is closed although neither pressure nor volume is constant. The products of the first set of reactions are themselves reactive and additional sets of reactions are initiated with their sets of heat and material transport properties. These cross phenomena continue to interact, the ultimate result being the gun firing as observed. The data traditionally obtained for such an event have been quite sparse and cannot be used to describe or even identify the phenomena themselves much less the cross phenomena. Whether or not non-equilibrium thermodynamics considerations would make significant inroads in generating accurate quantitative descriptions of combustion processes must await the development and employment of more advanced techniques for obtaining combustion data.

From all of the discussion preceding, it would appear that the chemical data needed for accurate modeling of the combustion process are spatial and temporal descriptions of heat and the various, important species produced during the reaction sequences. Since reactions are fast

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9. I. Prigogine, *Bull. Acad. Belg. C. Sci.* 31, 600 (1945).

10. R. Haase, *Thermodynamics of Irreversible Processes*, Addison-Wesley, Reading, MA (1969).

and the reaction zones are small, a high level of resolution is required in these spatial and temporal descriptions. The chemical data needed, however, are only a portion, and possibly a small portion, of all of the data required for accurate modeling of practical propellant combustion since, at the very least, the chemical data must be coupled with hydrodynamic processes that are taking place simultaneously. Limiting discussion only to the chemical reactions portion for purposes of simplicity, a formidable set of problems still emerges. Identity of many of the important species is not yet known and an accurate determination of the spatial, temporal and thermal properties of such a simple and stable product as nitrogen has not yet been made. It would, therefore, seem that the development and application of diagnostic methods capable of generating such data would substantially advance the state-of-the-art. Such spatial and temporal data are usually the products of investigations in reaction kinetics and the new diagnostic techniques that will be discussed subsequently are ones that seem especially suited to provide kinetics data. We have been very careful not to suggest that studies in reaction kinetics of propellants or propellant ingredients will "solve the combustion problem". We do feel, however, that such studies will make significant inroads and could, quite possibly, reduce the problem to one of manageable size.

In light of the magnitude and complexity of the problem, a word of caution is advised. It seems unrealistic to expect that a complete solution of the gun propellant combustion problem could be forthcoming within a reasonable time even if a major effort were expended toward such end. In order to utilize resources in a most efficient manner, close interaction between personnel acquiring combustion data and personnel developing, testing, and applying combustion models is mandatory. The paucity of available data and the difficulties anticipated in developing and employing suitable diagnostic techniques are such that priorities will be required in order to address those problems presently felt to be of greatest urgency. One approach to solution of this large and complicated problem is the continued acquisition, with some refinements, of gross, parametric data such as burning rates and gas evolution rates. We feel that this approach, although expeditious, is inadequate because such data cannot implement a quantitative description of the phenomena that are actually taking place. Furthermore, no refinements in such methods are foreseen that could result in the generation of adequate data. Since gross measurements are inadequate and are expected to remain so and complete description of the physical and chemical processes are realistically unattainable, a middle course is called for both in the acquisition of data and in the use to which such data will be put when acquired.

### III. COMBUSTION DIAGNOSTIC TECHNIQUES

The need for information about the identity of the important chemical species in the combustion process and, given their identity, the need

for spatial, temporal, and thermometric data about them was described in the preceding section of this report. We now address methods for obtaining such information. We will use the term "temperature" in these discussions although we will not use it in its correct, thermodynamic, meaning. Normally, temperature implies thermodynamic equilibrium. In our usage temperature will refer to a distribution of energy levels for a given atomic or molecular species with no inference of equilibrium so that a given chemical entity could exist simultaneously in some spatial region at several different temperatures. Temperature measurements will, therefore, be the determination of energy level populations. Our interest in identifying reaction products is increased by the fact that the identity of reaction products permits prediction of subsequent reaction. In this regard, knowledge of the energy state of the product is crucial since the same species may exhibit markedly different reactivity in different energy states.

We will briefly review combustion diagnostic techniques in current use although we will limit discussion to propellant combustion. New techniques will be discussed in light of their potential for generating the kind of data shown to be needed in Section II of this report. The new techniques will not be assessed in terms of scientific interest and accomplishment in developing the technique per se. A major phenomenological difference between propellant combustion and other types of combustion processes is the fact that fuel and oxidizer are homogeneously distributed on a macroscopic or possibly microscopic scale in a gun propellant so that mixing and reactant distribution will apply only to intermediate species that are produced during the course of reaction. Major diagnostic efforts have been devoted to the formation and distribution of fuel droplets and their reactions with air in hydrocarbon combustion studies, very little of which is probably applicable to gun propellant combustion diagnostics.

Potentially applicable diagnostic techniques fall into three, broad categories: those using probes, those using sampling methods, and those that involve various spectroscopic methods. Thermocouples have often been used for the determination of time-temperature profiles; other types of probes have also been used<sup>11</sup>. Probe measurements suffer from two fundamental deficiencies that limit their value to greater or lesser extents. The presence of the probe introduces a foreign material into the combustion zone and this material could, by its mere presence, strongly affect the combustion process. If this is the case, then the measurements made are not representative of the data desired. The validity of such measurements should be subject to meticulous scrutiny since inferences derived from probe data could be totally invalid. It should be pointed out that the more vigorous the combustion process, the greater the mechanical strength requirement placed on the probe. This can often mean that more massive and hence more severely perturbing probes are required in order to acquire data. A second and somewhat less severe deficiency deals with

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11. R. M. Fristrom in reference 3, pp. 287-317.

the size of the active area of the probe. The data obtained is the average over the active area of the probe. If this area is large relative to the region of reaction, the data recorded will be in error. In this regard, the reader is reminded of the very small size of the combustion zone in practical propellant combustion. Because of the limitations cited, the use of probes will not be discussed further in this report.

Sampling techniques involve the rapid removal of material from the region of reaction for subsequent analysis. Mass spectrometry is now being used to sample the decomposition products of laser-heated solid propellants<sup>12</sup>. Mass spectrometry can, in principle, detect any kind of molecule. However, in contrast to the non-intrusive nature of the laser techniques to be discussed later, the molecules to be detected by mass spectrometry must be extracted from the gas-phase process into a high vacuum chamber. If the process being studied is at atmospheric pressure or higher, extraction is non-trivial at best. Worse, perhaps, is the ever-present danger that the molecules that are detected are different from those in the process being studied. This can happen if chemical reactions continue to take place in the sampling process, or if clustering takes place as the sample is extracted (and cooled), or if the sampling process causes molecules to pass through a shock and be dissociated. Further, mass spectrometers sort by the ratio of  $m/e$ , the mass to the charge, so that singly-charged  $N_2$  and  $CO$ , both important in many combustion processes, are not separated except by the most sophisticated apparatus. Finally, mass spectrometry gives no information about the vibrational or rotational state of the molecule. For all these weaknesses, mass spectrometry has been used for years, is reasonably well understood, requires no understanding of spectroscopy, and is a very useful method for rapid determination of the species that will be encountered in a previously unstudied system.

The technique of multiphoton ionization mass spectrometry (MIMS) combines the sensitivity of mass spectrometry with the state specificity of laser excitation. This process was studied for a short time<sup>13</sup> before being halted by a lack of funding. In this method, two (or more) photons are used to excite the atom or molecule to a specific, electronically excited state, from which subsequent absorption into the photoionization continuum takes place. In the BRL apparatus, the ion is then extracted into a mass spectrometer and analyzed by mass and by the time it took to travel from the formation point to the detector. This arrangement gave excellent signal-to-noise ratios. While this technique is promising, there are several known questions to be answered before it could be applied. For example, MIMS has not yet been applied to molecules, such

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12. R. A. Beyer, "Molecular Beam Sampling Mass Spectroscopy of High Heating Rate Pyrolysis", BRL Report No. ARBRL-MR-02816, March 1978. (AD #A054328)
  13. T. D. Fansler, L. M. Colonna-Romano, and D. R. Crosley, "Mass Spectrometric Detection of Multiphoton Ionization", International Conference of Multiphoton Processes, Rochester, NY, June 1977.

as NO, nor has the problem with extraction from high gas pressures been worked out. There is no one that is working to apply MIMS to combustion diagnostics. MIMS has such excellent sensitivity that it deserves to be remembered.

The third category of diagnostic measurements involve techniques that are based on optical spectroscopy. All are non-intrusive, that is, they do not significantly perturb the reacting region being studied. Combustion diagnostic methods based on spectroscopy are currently receiving a great deal of attention for applications other than propellant combustion. Thus there are many techniques which should be considered. They include:

1. Rayleigh Scattering
2. Mie Scattering, including Laser Doppler Velocimetry (LDV).
3. Emission
4. Absorption
5. Laser-excited Fluorescence (LEF)
6. Optoacoustic Pulse Detection
7. Spontaneous Raman Scattering
8. Near-Resonance Raman Scattering (NRRS)
9. Inverse Raman Spectroscopy (IRS)
10. Coherent Anti-Stokes Raman Scattering (CARS)
11. Other Non-Linear Spectroscopic Techniques

Two recent reviews have been most helpful, an analysis of the usefulness of modeling and diagnostics by Hartley, et al.,<sup>14</sup> and a review of several diagnostic techniques by Eckbreth, et al.<sup>15</sup>

As far as diagnostics were concerned, Hartley, et al., addressed LDV, Raman Scattering, LEF and scattering off particles (Mie scattering). CARS was mentioned, but it was not judged useful at that time because of its lack of development.

Eckbreth, et al.,<sup>15</sup> did a splendid job of reviewing Raman and fluorescence techniques in a report for the EPA. They considered most of the techniques listed in the previous section in detail. They concluded that LEF and CARS have excellent potential as complementary diagnostic techniques for practical combustion studies.

Rayleigh Scattering. Rayleigh scattering of light by molecules is an elastic process, so that the wavelength is unchanged. Rayleigh scattering is shown in Figure 3. The cross section of the process is wavelength dependent, and that is responsible for the blue color of the sky. Until recently, Rayleigh scattering did not seem to depend on the

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14. D. Hartley, M. Lapp, and D. Hardesty, *Physics Today*, pp. 36-47, December 1975.

15. A. E. Eckbreth, P. A. Bonczyk and J. F. Verdieck, *Appl. Spec. Rev.* 13 (1), 15, (1977).

molecular species doing the scattering, so while it could be used to measure the total gas density it could not be used to obtain measurements of individual species. Recently, however, Chan and Daily<sup>16</sup> have found that the signal from Rayleigh scattering is enhanced near an absorption resonance. This near-resonance Rayleigh scattering was shown to be useful in obtaining a spatial plot of a combustion participant under high-pressure conditions that hampered fluorescence measurements.

Measurements using Rayleigh scattering suffer from interferences from Mie scattering and scattering off windows and other solid objects. Rayleigh scattering itself interferes with fluorescence measurements.

Except in very clean systems, Rayleigh scattering has not seem appropriate for combustion measurements. The effect of Chan and Daily's work on this conclusion remains to be seen, however.

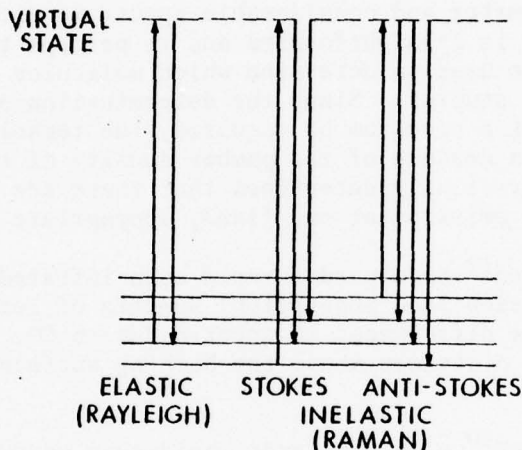


Figure 3. Light Scattering

Mie Scattering. Mie scattering is elastic scattering off particles, and it has been well studied over the years<sup>17</sup>. It can be used to probe combustion zones to determine the size distribution of particles. Measurements on practical systems will often be hampered by nonhomogeneous particle size and scattered light, however.

Mie scattering off particles can cause interference at the laser wavelength for fluorescence measurements, but it is easily controlled.

16. C. Chan and J. W. Daily, "Near-Resonance Rayleigh Scattering and Atomic Flame Fluorescence Spectroscopy", Tenth Material Research Symposium, Gaithersburg, MD, September 1978.

17. M. Kerker, The Scattering of Light, Academic Press, New York, (1969).

Mie scattering is the process used by Laser Doppler Velocimetry (LDV), which is sometimes called Laser Doppler Anemometry. LDV is a well-developed technique for measuring flow velocities. To insure uniform, spherical scattering centers, flows to be measured are usually seeded. Durst et al.,<sup>18</sup> have written an excellent book summarizing the theory and operation of LDV. Unlike newly-emerging laser-based techniques to be discussed later, LDV is well understood, and thus it can be implemented in a laboratory as a measurement technique without having to delve very deeply into the theory behind it. LDV equipment is available commercially, off the shelf, another mark of a technique which had made the transition to a useful technique.

Emission. The light which is spontaneously emitted from a combustion process comes from transitions that molecules make from a higher energy state to a lower state. The spectrum of the emitted light is characteristic of the molecules which are involved in the combustion process, and it can be analyzed to obtain the relative abundances of the excited state populations of the molecules. Sorting out the emissions takes a good spectrometer and considerable spectroscopic understanding. However, the process is straightforward and is perhaps the first technique which should be used to determine which molecules are participating in the process to be studied. Since the determination of a molecular species requires that a spectrum be acquired, the technique does not provide an instantaneous measure of the number density of the species, unless, of course, one has previously determined that there are no interferences and one measures the emission at one fixed, appropriate wavelength.

Lannon and Husted<sup>19</sup> have used a rapid-scan infrared spectrometer to obtain infrared emission (and absorption) spectra of leaded and unleaded propellant. They saw differences in spectra due to CO, hydrocarbon, H<sub>2</sub>O, and CO<sub>2</sub> at different distances above the burning surface and at different pressures.

Powell and Wilmot<sup>20</sup> also have made rapid-scan measurements of the flame zone of burning propellants. They obtained spectra which were characteristic of CO, NO, and CO<sub>2</sub>.

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18. F. Durst, A. Melling, and J. H. Whitelaw, Principles and Practice of Laser-Doppler Anemometry, Academic Press, NY (1976).
  19. J. A. Lannon and D. Husted, "The Fundamentals of Ignition and Combustion", I. W. May and A. W. Barrows, ed., BRL Report No. 1707, Vol. 1, pp. 217-250, April 1974.
  20. E. G. Powell and G. B. Wilmot, *Proceedings of the 14th JANNAF Combustion Meeting*, CPIA Publication No. 292, Vol. 1, pp. 163-180, December 1977.

Mal'tsev, et al.,<sup>21</sup> made emission studies of hexogen, a model mixed composition based on ammonium perchlorate and polymethylmethacrylate, and nitrocellulose. The studies were done in a closed bomb at pressures of 1 to 40 atm. Radical species were identified as a function of height above the burning surface; while the quality of the work is not up to close comparisons with combustion models, it certainly gives guidance about the species encountered. They saw OH, CH, CN, C<sub>2</sub>, NH, and final products characteristic of the radiation of hydrocarbon flames. The radiation of OH was relatively intense near the surface; the radiation of CH, CN, and C<sub>2</sub> exceeded the value one might expect in establishing thermodynamic and chemical equilibrium.

Dewilde and Crosley<sup>22</sup> are presently using emission (and absorption) to measure OH rotational distributions, from which rotational temperatures are deduced, in a flame. They have found a rotational temperature of about 2700K for OH in the secondary zone of an ethane/air flame; a thermocouple measurement at about the same location yielded 1400K. In the primary zone of a methane/air flame, 8500K was obtained for OH. These measurements demonstrate again<sup>23</sup> how slowly rotational energy is converted into translational energy in a flame and that there is a competition between rotational and electronic transfer.

Absorption. Just as each molecule emits at characteristic wavelengths, so do molecules absorb light quanta at discrete wavelengths. Thus one can determine the molecular components of a system by illuminating it with a continuum of frequencies or a varying frequency monochromatic light, noting the absorptions, and matching them to known molecules. The study of absorption is complementary to emissions measurements in that it yields the relative abundances of the ground states of the molecules involved. Several of the emission efforts already mentioned include absorption work. Absorption measurements can be used for very sensitive probing of a system. It is a line-of-sight technique, however, so it is not as spatially precise as other techniques discussed here. Again, as with emission measurements, absorption studies are very useful for surveys to precede more careful measurements by more powerful techniques.

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21. V. M. Mal'tsev, A. G. Stasenko, B. A. Seleznev and P. F. Pokhil, *Frizika Goreniya i Vzryva*, 9, 220 (1973).
  22. M. A. Dewilde and D. R. Crosley, "Measurement of Rotational Distributions Within OH in Flames", Tenth Materials Research Symposium, Gaithersburg, MD, September 1978.
  23. A. G. Gaydon, *The Spectroscopy of Flames*, John Wiley and Sons, New York (1974).

Quite recently, laser-based absorption measurements have been made on the primary thermal decomposition products of HMX<sup>24</sup>. At this writing the data are still being analyzed, but the results are consistent with older mass spectrometer measurements and provide an independent calibration of the relative amounts of the products observed with each technique.

Tunable diode lasers promise easier absorption measurements of the species in emitting systems in the future<sup>25</sup>, for these lasers can generate such power at a particular wavelength that their equivalent "temperature" is much hotter than that of the system under study. While tunable diode lasers are available commercially, they are new instruments and are not yet used for routine measurements. Absorption measurements using tunable diode lasers hold great promise for the future, however, and the idea should not be forgotten.

Laser Excited Fluorescence. Laser excited fluorescence (LEF)<sup>26-28</sup> continues to show promise as a sensitive, selective detection and measurement technique for some gases<sup>14</sup>. Fortunately, the particular gases that are appropriate for LEF are important transient constituents in combustion processes; OH, CN, CH, NH, C<sub>2</sub>, etc.<sup>21</sup> LEF is used to detect these molecules by exciting them to a selected state and then detecting the re-radiated fluorescence.

Figure 4 is applicable to LEF, and should aid one's understanding of the physical process involved. The laser excites the molecule from a particular electronic state of the molecule to a different electronic state with a photon of energy  $E_2-E_1$ . Some time later, the molecule emits radiation of energy  $E_2-E_3$  (fluorescence) and returns to the original electronic state of the molecule. If it fluoresces from the same vibrational and rotational level to which it was excited down to the vibrational and rotational level from which it was excited, the fluorescence is "resonant". Rayleigh scattering, Mie scattering, and scattering off surfaces interfere with resonance fluorescence, so typically one studies

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24. R. A. Beyer, *private communication*.
  25. K. G. P. Sulzmann, J. E. L. Lowder and S. S. Penner, *Comb. Flame* **20**, 177 (1973).
  26. J. E. Allen, Jr. and D. R. Crosley, *Bull. Amer. Phys. Soc.* **22**, 76 (1977).
  27. J. E. Allen, Jr., W. R. Anderson, and D. R. Crosley, "Franck-Condon Factors in the B-X System of S<sub>2</sub>", *Proceedings of the Symposium on Molecular Structure and Spectroscopy*, Columbus, OH, June 1977.
  28. J. E. Allen, Jr., W. R. Anderson, D. R. Crosley, and T. D. Fansler, "Energy Transfer and Quenching Rates of Laser-Pumped Electronically Excited Alkalies in Flames", *Seventeenth Symposium (International) on Combustion*, Leeds, August 1978.

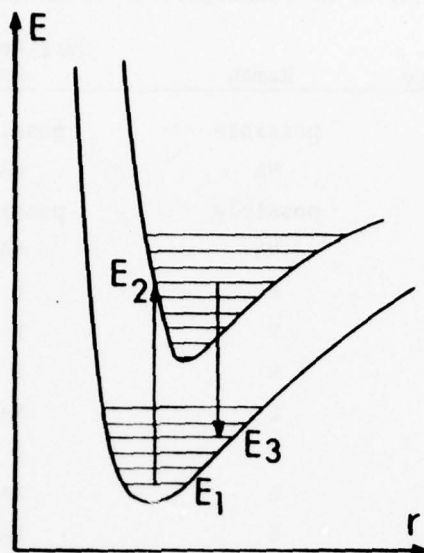


Figure 4. Fluorescence Energy Diagram

the fluorescence to other vibrational and rotational levels of the final state of the molecule.

To be amenable to study with LEF, a molecule must have a known emission spectrum. Further, the molecule must have transitions which can be excited by available lasers. The molecule must leave the excited state primarily by fluorescing rather than dissociating, for example. For quantitative measurements of the number density of the molecule, one must also know the rate at which the excited state radiates. Table I, due to Eckbeth, et al.,<sup>15</sup> includes a listing of candidate molecules and an assessment of the applicability of LEF to their study.

At this writing, OH is the only molecule which has an emission spectrum well-enough characterized for quantitative measurements. Thus one must do some background emission studies on each other molecule to be studied. Fortunately, LEF work is appearing in the literature in ever-increasing amounts. A second disadvantage of LEF, as far as its application to practical systems is concerned, is that the fluorescence is emitted into  $4\pi$  steradians of space, not in a coherent beam. Thus, efficient signal collection requires that some optics be mounted close to the system under study, and for a system that could explode, for example, this could be a problem.

Allen, et al.,<sup>28</sup> have recently observed, for the first time, multiphoton excitation in a flame. They used two-photon excitation to populate the 3D, 5S, and 4D states of Na. Direct one-photon transitions to any of these states from the 3S state are parity-forbidden.

TABLE I. SUMMARY OF APPLICABILITY OF TECHNIQUES

Species	Fluorescence	Raman	Near-Resonant Raman	CARS
C	NA	possible	possible	possible
H	NA	NA	NA	NA
O	NA	possible	possible	possible
N	NA	NA	NA	NA
C <sub>2</sub>	G	E	E	E
CH	E	P	P	P
CN	E	P	P	P
CO	NA	E	NA	E
CS	F	P	P	P
H <sub>2</sub>	NA	E	NA	E
N <sub>2</sub>	NA	E	NA	E
NH	E	F	P	G
NO	E	G	P	G
O <sub>2</sub>	NA	E	NA	E
OH	E	G	G	G
CH <sub>2</sub>	NA	?	NA	?
CH <sub>3</sub>	NA	?	NA	?
CH <sub>4</sub>	NA	E	NA	E
C <sub>2</sub> H <sub>2</sub>	?	E	NA	E
C <sub>2</sub> H <sub>4</sub>	NA	E	NA	E
C <sub>2</sub> H <sub>6</sub>	NA	E	NA	E
C <sub>6</sub> H <sub>6</sub>	E	G	P	G
C <sub>10</sub> H <sub>8</sub>	E	G	F	G
C <sub>14</sub> H <sub>10</sub>	E	G	G	G
CO <sub>2</sub>	NA	E	NA	E
CH <sub>2</sub>	G	G	NA	G
HCO	?	?	?	?
HCN	F	G	NA	G
H <sub>2</sub> O	NA	E	NA	E
NH <sub>2</sub>	F-G	G	G	G
NH <sub>3</sub>	NA	E	NA	E
NO <sub>2</sub>	P	G	G	G
NO <sub>3</sub>	?	?	?	?
SO <sub>2</sub>	G	E	P	G
SO <sub>3</sub>	?	?	?	?

E Excellent, G Good, F Fair, NA Not applicable, ? Not enough information or untried.

Multiphoton excitation is then a potentially useful adjunct to single-photon LEF, for it permits excitation of states to which transitions are parity-forbidden and also states which are inaccessible with one photon from the available laser. Further, several photons could be used to excite states lying too high in energy to be reached even by one photon of frequency-doubled laser light.

The potential for productive application of LEF to practical systems has continued to motivate work of a more practical, less spectroscopic, nature. Wrobel and Pratt have reported<sup>29</sup> very nice spatially and temporally resolved measurements on trace quantities of Na in a turbulent propane diffusion flame. Interferences from particle scattering were successfully suppressed. Laser beam modulation and phase sensitive detection were used to suppress strong flame emission.

While the molecule is in the excited state, collisions can cause changes in both vibrational and rotational levels, adding considerable complexity to the fluorescence signal and greatly complicating a determination of the number density of the molecules. These collisionally-induced energy changes, which include chemical reactions, cause "quenching", an increase in the total decay rate of the originally excited state. Quenching is an especially serious problem in practical, combustion regimes, where the collision partners may not be known, much less all of the energy transfer rates. Contending with quenching has become the object of the most intense research on the technique of LEF.

If a laser source with sufficient intensity is used, one should be able to saturate the transition, that is, excite many of the selected molecules within the laser target area to a particular excited level. Under those conditions, the number density of the excited state is simply related to the number density of the ground state, and the fluorescence signal becomes independent of quenching rates and even incident laser power<sup>30</sup>. At this writing, OH,<sup>16</sup> CH,<sup>31</sup> CN,<sup>32</sup> C<sub>2</sub>,<sup>32</sup> and NH<sup>33</sup> seem to be

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29. N. H. Wrobel and N. H. Pratt, "Laser Induced Sodium Fluorescence Measurements in a Turbulent Propane Diffusion Flame", *Seventeenth Symposium (International) on Combustion*, Leeds, August 1978.

30. J. W. Daily, *Appl. Opt.* **15**, 955 (1976).

31. A. C. Eckbreth, P. A. Bonczyk, and J. A. Shirley, "Investigation of Saturated Laser Fluorescence and CARS Spectroscopic Techniques for Combustion Diagnostics", EPA-600/7-78-104, United Technologies Research Center, Hartford, CT, June 1978.

32. A. P. Baronavski and J. R. McDonald, *J. Chem. Phys.* **66**, 3300-3301, (1977).

33. D. R. Crosley, private communication.

able to be saturated. One encouraging sign in this battle is that the power required to saturate CN and CH<sup>30</sup> turned out to be much less than had been estimated<sup>15</sup>. Certainly the last word is not in on saturation, as Daily's<sup>34</sup> paper on the effects of the Gaussian spatial nature of a real laser beam demonstrates. However, for the interesting radicals at least, the achievement of saturation seems possible and keeps LEF in the running as the single most valuable technique for investigating transient species in combustion processes.

Opto-Acoustic Pulse Detection. A newly observed opto-acoustic phenomenon, laser-generated opto-acoustic pulses, has been observed in a flame<sup>35</sup>. The technique can be used to measure the speed of sound at a particular location in a flame; if the gas composition is well enough known the information can be used to deduce the gas temperature. It may also be a suitable detector for selective absorption diagnostic measurements. In this mode, the technique holds promise as a complement or substitute for LEF for those situations in which the excited molecule does not fluoresce, either because of quenching, reaction, or rapid transfer to some non-fluorescing state<sup>26</sup>.

Opto-acoustic pulses are formed when a pulsed laser excites selected molecules, in the manner of LEF. However, here the energy is transferred from electronic energy (presumably through vibrational energy) to translational energy, that heats the gas in the small region of excitation, and a shock wave is generated as the region equilibrates. The shock wave can be heard by an observer in the laboratory, and has since been used for tuning the laser to the wavelength for absorption. Some characteristics of the process were established<sup>35,36</sup> before the work was halted by lack of funding. What is important here is that this is a way to detect the selective deposition of energy in a particular molecule (and thus detect the molecule) which is not adversely affected by quenching.

Spontaneous Raman Scattering. Spontaneous Raman Scattering (SRS) is a very selective technique for detection of atoms and molecules. Reference to Figure 3 shows energy level transitions which are a lot like LEF, except that the upper state is a virtual state and both the "absorption" and "emission" occur simultaneously in this scattering process and are thus immune to quenching. Like LEF, the scattered photons come off into 4 $\pi$  steradians, so some optics are necessary near the system under study.

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34. J. W. Daily, *Applied Optics* 17, 225-229 (1978).

35. J. E. Allen, Jr., W. R. Anderson, and D. R. Crosley, *Optics Letters*, 1, 118-120 (1970).

36. W. R. Anderson, J. E. Allen, Jr., T. D. Fansler, and D. R. Crosley, "Laser-Generated Opto-Acoustic Pulses in an Atmospheric Pressure Flame", *Proceedings of the Tenth Materials Research Symposium*, Gaithersburg, MD, September 1978.

If the scattered photon is of lower energy than the exciting photon, the scattering is "Stokes", if the scattered photon energy is of higher energy (in a hot system, for example) the scattering is "anti-Stokes". This technique has been widely applied to studies of clean flames. It suffers only one major problem - the cross sections are very small. Typically, the collected Raman to laser energy ratio is about  $10^{-14}$  in a flame<sup>15</sup>. Thus, in practical combustion systems, the achievable signal to noise ratio is just too low. The review report of Eckbreth et al.,<sup>15</sup> has a very complete analysis of this technique.

Near-Resonance Raman Scattering. Near-resonance Raman scattering (NRRS) is the term applied to spontaneous Raman scattering when the virtual state is close to a real, bound state. The appeal of NRRS is that as the scattering approaches a bound state, the cross section increases as much as a factor of  $10^6$ . Such a signal enhancement in a technique with so many other advantages make NRRS obviously worth considering in detail.

Now NRRS (with its near-instantaneous emission) and LEF (with its emission characteristic of the bound, excited state) becomes very similar as the laser wavelength is tuned toward the resonance wavelength. The question to be answered is: is there any difference in these two techniques? Since LEF is subject to quenching but NRRS (as a scattering process) is not, quenching studies were at first used, but the results were ambiguous. Williams et al.,<sup>37</sup> showed, with temporally resolved scans, that LEF and NRRS have two discrete, not-continuously mixed time constants, one (LEF) characteristic of the molecular state and one (NRRS) characteristic of the laser pulse. They found no exponentially decaying component which depends on the frequency difference between the exciting pulse and resonance.

That paper<sup>37</sup> prompted a flurry of theoretical activity, with several groups trying to explain the observation "correctly". Mukamel and Jortner<sup>38</sup> put forward a quantum mechanical treatment of time resolved resonant and near-resonant light scattering from a molecular system. Their time resolved decay pattern was characterized by just two types of life times, while the off-resonance energy parameter affected the total intensity and, in some cases, the relative intensities of the different decay components.

Courtens and Szöke<sup>39</sup> treated near-resonance Raman scattering, resonantly enhanced two-photon absorption, and resonance fluorescence in a unified and "simplified" way. Their conclusions agreed with the measurements. Their paper contains an unusually good list of references.

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37. P. F. Williams, D. L. Rousseau, and S. H. Dworesky, *Phys. Rev. Lett.* 52, 196-199 (1974).

38. S. Mukamel and J. Jortner, *J. Chem. Phys.* 62, 3609-3615 (1975).

39. E. Courtens and A. Szöke, *Phys. Rev. A* 15, 1588-1603 (1977).

Rousseau and Williams<sup>40</sup> considered near-resonance Raman scattering from a homonuclear diatomic molecule in detail, both with measurements and with calculations using "simple" perturbation theory. Their calculations based on general theories describe correctly the experimental data.

Then there is the interesting paper by Raymer and Carlsten<sup>41</sup>. They observed collisional redistribution of laser light scattered by a three-level atom, thallium, in the presence of argon. The two observed spectral components correspond to Raman scattering and collision-induced fluorescence. They see growth of both components from spontaneous to simulated scattering as the laser intensity is increased; that is the output from each increased at a rate more than proportional to the laser power. That would imply that higher-power lasers will, in the future, lead to significant improvements of the signal-to-noise ratio.

Immune as it is to quenching, NRRS still has several difficulties which argue against its application. As with LEF, there are no lasers available with which to study the majority species in combustion processes. The transition back and forth from LEF to NRRS takes place in a few thousandths of a nm, so one must use a very stable laser with very narrow line width to be able to obtain unadulterated NRRS. (This argues against a "simple" check of NRRS with an existing LEF apparatus.) Third, the amount of enhancement to be expected varies from calculation to calculation, but it is likely to be different for each rotational line excited. Thus, in contrast to SRS, in which the entire vibrational ensemble can be sampled, for NRRS only one line at a time can be used, further reducing the total signal.

Thus we see that laser development may well vault NRRS back into the limelight sometime in the future, but the above disadvantages coupled with a lack of any present application to combustion systems combine to argue against NRRS at this time.

Inverse Raman Spectroscopy. Inverse Raman spectroscopy (IRS) is a method of detecting molecules which seems now best suited to condensed phases. The BRL work on IRS was begun by VonHolle<sup>42</sup>, and it was continued by Crosley and Schroeder, who are writing a report on the work carried out thus far<sup>43</sup>.

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40. D. L. Rousseau and P. F. Williams, *J. Chem. Phys.*, **64**, 3519-3537 (1976).

41. M. G. Raymer and J. L. Carlsten, *Phys. Rev. Lett.* **39**, 1326-1329, (1977).

42. W. VonHolle, "The Application of Inverse Raman Spectroscopy to Chemical Decomposition in Energetic Systems (U)", BRL Memorandum Report No. 2607, March 1976.

43. D. R. Crosley and M. A. Schroeder, "Inverse Raman Spectroscopy", manuscript in preparation for publication as a BRL Report.

IRS, and other Raman techniques, makes use of the non-linear parts of the molecular polarizability. Specifically, the third-order susceptibility gives rise to a number of three-wave and four-wave mixing processes, including IRS. The details of the signal levels that can be expected have been worked out elsewhere<sup>43</sup>. Here, let us consider a phenomenological description of what is happening by considering Figure 5. The radiation  $\nu_L$  is typically from a high-power ruby laser, and  $\nu_A$  from a dye laser, which is pumped by doubled ruby light. The dye laser is used to irradiate the molecules with a continuum. A fast laser pulse then induces the molecules to absorb from the dye continuum (while simultaneously emitting, into  $4\pi$  steradians Raman-shifted light). Thus the signal is seen as absorption from a continuum, and a coherent continuum at that. The detector can be quite far from the system under study and the process is essentially instantaneous, making it applicable for rapidly-occurring processes like deflagration or even detonation.

IRS has been criticized because of low sensitivity and problems with signal detection. The use of an optical multichannel analyzer (OMA) at the BRL has significantly improved problems with signal detection. The technique does have low sensitivity for low pressure, gas phase studies, but continues to look very promising for studies at the much higher densities of interest to ballistics.

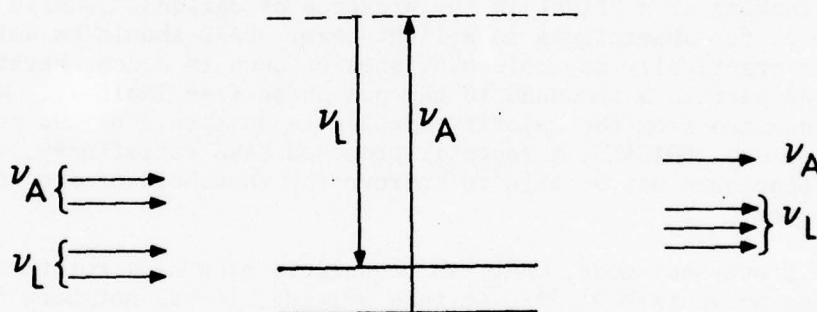


Figure 5. Inverse Raman Spectroscopy

Coherent Anti-Stokes Raman Scattering. Coherent anti-Stokes Raman scattering (CARS) is seen as the clear choice for detecting and measuring major molecular species in gas-phase combustion diagnosis of practical systems<sup>15</sup>. A feeling for the physics of the process can be gained from Figure 6. Here we see several transitions which are explained sequentially, but all of which happen simultaneously. A photon of energy  $h\nu_L$  is absorbed by the molecule, which is stimulated by a photon of energy

$h\nu_2$  to emit (incoherently) a photon of energy  $h\nu_2$ ; the molecular further absorbs a photon of energy  $h\nu_1$  and emits a coherent photon of energy  $h\nu_3$ . Note that if the laser which emits at  $\nu_2$  is pumped by the one at  $\nu_1$ , (a ruby laser pumping a dye laser, for example) the CARS signal goes as the cube of the original laser power.

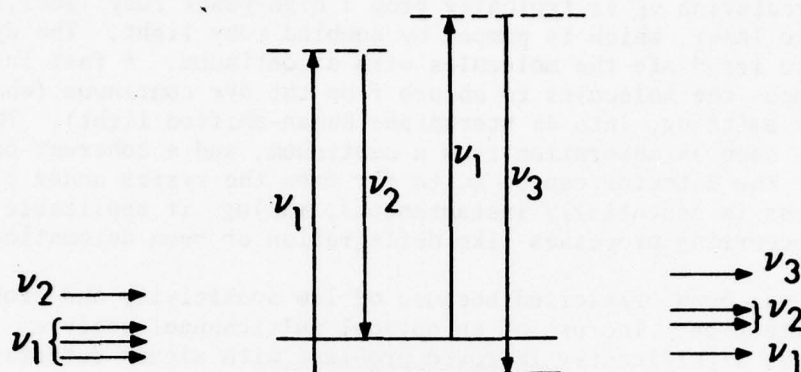


Figure 6. Coherent Anti-Stokes Raman Scattering (CARS)

CARS has the advantage that IRS had - a coherent output beam. It has an additional nice feature, in that the signal is an emission, so one is looking at a "light in the presence of darkness", while for IRS one looked for absorptions in a light beam. CARS should be able to be used for practically any molecular species down to a concentration of about one part in a thousand in the gas phase (see Table I). Non-resonant CARS generated from the majority species gases should be the principal noise source. BOXCARS, a recently proposed CARS variation<sup>44</sup>, and/or other techniques may be able to improve the threshold of species able to be detected.

In a one-shot mode, CARS can be used to make nice rotational temperature measurements<sup>15,31,45</sup>. At this writing, it has not been evaluated in the context of other measurements which yield more than one temperature at a single point in a flame<sup>22,23</sup>.

CARS requires one to start with a high peak power laser, say ruby or neodymium, where neodymium seems preferable at this time. The technique uses much the same equipment as IRS. The practical use of CARS, like many of the techniques mentioned, requires some commitment to the

44. A. C. Eckbreth, *Appl. Phys. Lett.* **32**, 421 (1978).

45. W. B. Roh, "Coherent Anti-Stokes Raman Scattering of Molecular Gases", AFAPL-TR-77-47, Systems Research Laboratories, Inc., Dayton, Ohio, August 1977.

study of the technique. One way to do this is the method at AFAPL, where they have two CARS apparatuses; one for research on the technique exploring temperature and pressure effects, and one for use on a real combustor.

Because CARS has so many advantages, because some appropriate equipment and personnel exist already at the BRL, and especially because combustion efforts are underway at both AFAPL and at United Technologies Research Center (UTRC), CARS is an obvious candidate for study at the BRL.

Other Non-Linear Processes. Raman-induced Kerr effect spectroscopy (RIKES) is similar to IRS, in that a high-power monochromatic pumping laser and a broad-band probe laser are used to produce birefringence at the Raman frequencies. Resonant enhancement occurs when the frequency differences between probe and pump frequencies equal the vibrational resonances of the molecule being detected. The signal-to-noise ratio from RIKES is limited by the quality of the optics used;  $10^6$  to 1 is the target for today's optics. The technique is being studied by its originator, Hellwarth, at the University of Southern California,<sup>46</sup> and VonHolle at the Lawrence Livermore Laboratory. It has a high potential, but a high risk also. No one is yet applying RIKES to combustion systems.

Stimulated Raman scattering is very much like spontaneous Raman scattering except that very intense lasers are used. At high pressures, with high laser power the Raman signal can be made to increase exponentially with laser power. Moreover, the photons emerge in a coherent beam. Unfortunately, this technique only applies to a few major-species gases. It is not being applied to combustion research as far as is known.

High-order Raman spectral excitation studies (HORSES) deserves comment, perhaps just because of its acronym. In a CARS apparatus, higher-order signals are also observed which correspond to four-wave mixing. They are low in power, and they are unlikely ever to be useful for combustion research.

#### IV. EXPERIMENTAL CONSIDERATIONS

Since both a need for detailed combustion data and a variety of techniques for obtaining such data have been discussed, a number of practical problems will now be briefly addressed. No attempt will be made to design specific experiments but rather attention will be drawn to methods and equipment common to many of the techniques.

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46. D. Heiman, R. W. Hellwarth, M. D. Levenson and G. Martin, *Phys. Rev. Lett.* 36, 189 (1976).

In all discussions of combustion, emphasis has been placed on the practical combustion of gun propellants. Whether studies are to be carried out on finished propellants, propellant components, or model compounds, essentially the same constraints apply. All such materials are quite energetic and therefore potentially dangerous to personnel and equipment. In addition, studies are to be conducted at elevated pressures which enhances the potential danger. Chambers in which combustion will take place must be able to withstand the temperatures and pressures anticipated and, in use, must be isolated from personnel and delicate equipment. Optical measurements require windows that are transparent at the light frequencies that will be involved and must remain so for the duration of the measurement. Since the optical measurements in question are to be rather sensitive spectral determinations, a number of properties in addition to transparency must be specified for such windows. These include compositional uniformity, flatness, parallelism of faces, and, if more than one window is required, alignment. If the use of high intensity lasers is envisioned, optical breakdown of the windows must also be considered as well as laser induced fluorescence and phosphorescence that is occasionally observed. When coupled with temperature and pressure requirements, only two materials remain available for use as optical windows, namely quartz and sapphire. Of these, sapphire is much preferred because of its superior physical, chemical, and optical properties. Window size is, of course, a major factor in determining operational pressures of a combustion chamber. Conventional scattering as well as laser excited fluorescence are isotropic processes and sensitivity will be strongly dependent on light collection solid angle which, in turn, is dependent on window size. The several coherent processes described are anisotropic, making possible high sensitivity with small diameter windows. This problem is addressed in the combustion literature generally but is not given very strong emphasis. The problems unique to high pressure combustion that are inherent in practical gun propellant combustion studies make chamber window considerations a much more critical experimental constraint.

It is assumed that many of the linear optical techniques that appear viable will make use of laser light sources. All of the non-linear methods require lasers. In both cases, a commonality of equipment seems evident. Lasers are available either as pulsed or continuously operating devices, the very high power levels being available only in pulsed lasers. Laser light is available over a fairly wide frequency range. The range of frequencies available at very high intensities is limited and presently restricts application of a number of the techniques discussed. Some of the diagnostic methods, such as laser excited fluorescence, require light at specific frequencies whereas others, such as Raman scattering, do not. Where specific frequency or a fairly broad range of frequencies are required, dye lasers are the sources of choice. Some modest collection of pulsed and CW lasers, operating over a reasonable range of frequencies and power levels would permit investigation of a number of diagnostic methods. In some cases, more than one method could be employed simultaneously, for example, fluorescence and CARS. It should also be pointed

out that in techniques where two light beams are required such as inverse Raman and CARS, only one laser is required since a portion of the beam can be used to pump a dye thereby providing the second light beam.

Several of the techniques will be illustrated with diagrams in which a number of considerations mentioned are shown. Figure 7 shows laser excited fluorescence experimentation.

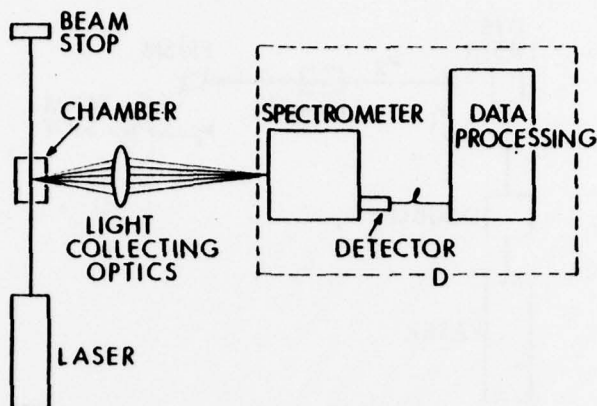


Figure 7. Laser Excited Fluorescence

The chamber shown contains three windows and is, therefore, useable for all of the techniques to be described subsequently. The equipment in the portion of the figure marked "D" will, with slight modifications, also be used repeatedly. Since LEF is an isotropic process, light collecting optics will be required. They are shown in the figure simply as a lens but will, in fact, probably be substantially more sophisticated and complex. The proximity of such optics to the combustion chamber will pose serious experimental difficulties.

An array for inverse Raman spectroscopy is shown in Figure 8. The laser shown is a very high intensity, pulsed laser and is useable, but not necessary, in all of the other methods using lasers.

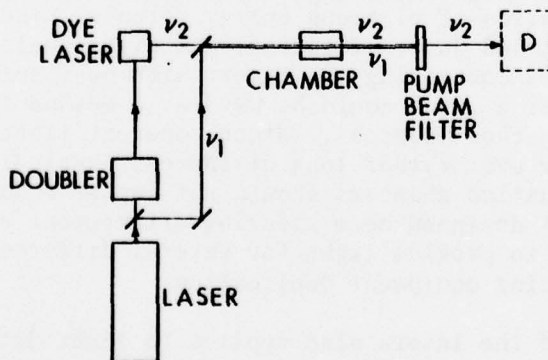


Figure 8. Inverse Raman Spectroscopy

The detector to be used for IRS work measures absorption rather than emission. It should also be noted that  $\nu_1$ , in the figure is of lower frequency than  $\nu_2$ , a point that will be mentioned further in discussing CARS.

A CARS array is shown in Figure 9.

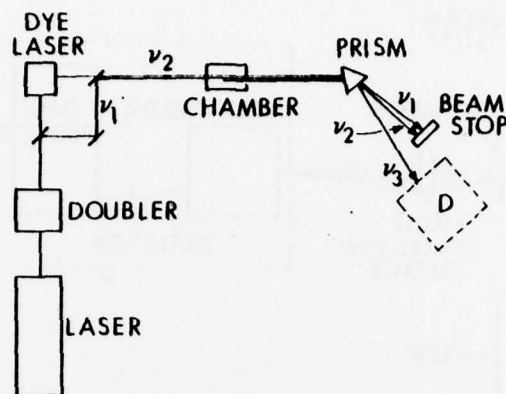


Figure 9. Coherent Anti-Stokes Raman Spectroscopy

The pumping beam,  $\nu_1$ , is now of higher frequency than  $\nu_2$ . The three beams emerging from the chamber in Figure 9 are rather easily separated, a simple prism being quite adequate for the purpose. The CARS spectrum of gaseous nitrogen nicely illustrates this point. Using a pump beam at  $5320\text{\AA}$  (green) and a Stokes beam at  $6073\text{\AA}$  (orange), the CARS signal emerges at  $4733\text{\AA}$  (blue).

Lasers of the sort envisioned for use in these studies are commercially available and are stable and dependable devices. They are, however, scientific instruments requiring care and proper handling if they are expected to function as desired and, as such, are not suited to a hostile environment. They should not be in close proximity to combustion chambers or other sources of vigorous energy release. They should also be isolated from dirt and dust, vibration, and high levels of acoustic noise. A central area containing the lasers with beam selection and steering to the reaction sites could be used as a method for safely and efficiently utilizing these sources. Since coherent light beams do not diverge significantly over rather long distances, physical separation of the lasers from combustion chambers should not impose undue experimental difficulties. A well designed beam steering arrangement also permits the use of one laser to provide light for several different experimental arrays, thereby reducing equipment duplication.

The isolation of the lasers also applies to light detectors and data recording and processing equipment. The problem of sensitivity and the

extraction of small signals from background noise has been repeatedly mentioned as a potentially serious problem in a number of the diagnostic techniques discussed. It seems reasonable to assume that the detection equipment needed will be quite complex possessing high sensitivity and extremely high noise rejection. Signal averaging, a widely used method of extracting small signals from background, is probably not available for exploitation for several reasons. A fundamental assumption in all signal averaging techniques is that the signal is repetitive in a controlled manner whereas the background noise is random. Propellant combustion at elevated pressures is quite rapid and the probability of generating a number of repetitive signals is small. Secondly, the supposition that the event under investigation is not changing with time so that repetitive signals are indeed repetitions of the same process, has not been experimentally demonstrated. It is doubtful if such is, in fact, the case, a major goal of the investigations being a temporal description of the combustion process. The non-availability of signal averaging places a much more severe requirement on detection equipment and it is expected that the development of suitable detection techniques will be a major portion of the overall effort in a diagnostics program.

A number of ancillary investigations of propellant phenomena become feasible at small cost and effort if diagnostic experimentation of the sort described is being conducted. Laser ignition studies are an obvious example but a number of other studies also come to mind. Visualization of the combustion process generally and regression of the propellant surface specifically has been attempted in the past with varying degrees of success. The presence of smoke, optically opaque gases, and the intense flame luminosity are major interferences in such studies. The use of intense, monochromatic illumination in visualization studies should greatly reduce such interferences. Velicometry measurements are currently being made<sup>18</sup> with excellent accuracy and precision using lasers. The use of laser holography for the measurement of thermal gradients and heat transfer prior to ignition is another technique that should result in important information about the ignition process and the earliest stages of propellant reaction. The several examples cited are, by no means, an exhaustive list of ancillary measurements.

## V. CONCLUSIONS AND RECOMMENDATIONS

The only conclusions that can be drawn from this study are that our present understanding of gun propellant combustion under practical conditions is inadequate, and that experimental investigations are called for to improve and expand our understanding of the subject. Accepting these conclusions, we find that several, newly developed, diagnostic techniques are capable of providing some of the needed, fundamental information. We recommend that several of these techniques, namely laser excited fluorescence, inverse, and coherent anti-Stokes Raman spectroscopy, be exploited toward this end and that such techniques be used in conjunction with, rather than in place of, presently ongoing studies.

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